

FACILITY FORM 65	N65-88359	
	(ACCESSION NUMBER)	(THRU)
	21	None
	(PAGES)	(CODE)
	CR-67113	
	(NASA CR OR TMX OR AD NUMBER)	(CATEGORY)

THE GAS PHASE CHEMILUMINOUS REACTIONS OF OZONE

A. SHARMA

J. P. PADUR



SCIENTIFIC REPORT NO. 3

CONTRACT NO. NASw-985

PREPARED FOR
NATIONAL AERONAUTICS AND SPACE ADMINISTRATION
HEADQUARTERS
WASHINGTON 25, D. C.

AUGUST 1965

GCA Technical Report 65-20-N

THE GAS PHASE CHEMILUMINOUS REACTIONS OF OZONE

A. Sharma and J. P. Padur

SCIENTIFIC REPORT NO. 3

Contract No. NASw-985

August 1965

GCA CORPORATION
GCA TECHNOLOGY DIVISION
Bedford, Massachusetts

Prepared for
NATIONAL AERONAUTICS AND SPACE ADMINISTRATION
Headquarters
Washington 25, D. C.

TABLE OF CONTENTS

<u>Title</u>	<u>Page</u>
INTRODUCTION	1
EXPERIMENTAL	3
OBSERVATIONS AND DISCUSSIONS	11
CONCLUSIONS	19
REFERENCES	21

LIST OF ILLUSTRATIONS

<u>Figure</u>	<u>Title</u>	<u>Page</u>
1	Medium pressure reaction system.	4
2	Low pressure reaction chamber.	5
3	Block diagram of complete apparatus for observation of chemiluminescence.	6
4	Ozone handling system.	7
5	An arrangement for transferring organometallic liquid.	9
6	The spectra of chemiluminescence produced during the reaction of nitric oxide with ozone and atomic oxygen.	14

THE GAS PHASE CHEMILUMINOUS REACTIONS OF OZONE

By A. Sharma and J. P. Padur
GCA Corporation, GCA Technology Division

INTRODUCTION

The chemical reactions of ozone with several compounds and particularly with organic compounds have been extensively studied. Bailey [1] has reviewed the previous work. Information regarding the gas phase chemiluminous reaction of ozone is very poor. Bernanose and Rene [2] have collected indicative information about the chemiluminescent reactions of ozone. It has been reported [3 - 6] that in contact with ozone, certain metalloids (iodine, sulfur, phosphorus, sodium and thallium) show their characteristic chemiluminescence. The chemiluminescence produced during the mixing of some inorganic compounds (hydrogen sulfide, oxygen compounds of nitrogen, phosphorus trioxide, carbon monoxide and zinc sulfide) and ozone has been observed [6 - 15]. The production of chemiluminescence has also been reported [16 - 21] during the reaction of ozone with hydrocarbons or their heterocyclic analogs (benzene, thiophene, ethyl alcohol, polyphenols in aqueous or organic solutions such as resorcinol, hydroquinon, pyrogallol, pyrocatechol and phloroglucinol; glucoside aesculin, chlorophyll, some dyes; hydrazides like luminol in alkaline solution). This early information regarding the chemiluminescent reactions of ozone is mostly qualitative. Moreover, the conditions under which the chemiluminescence is observed are not definitely specified. Recently, more definite information regarding the gas phase chemiluminescent reactions of ozone with nitric oxide [22], sulfur monoxide [23] and hydrogen atoms [24] is available.

We have surveyed the gas phase chemiluminescent reactions of several compounds with ozone at room temperature and at a pressure of about 1 mm Hg. It has been found that only a few of the above-mentioned compounds produce chemiluminescence during the mixing of their vapors with ozone under the above conditions. The evidence of some new chemiluminescent reactions of ozone has also been obtained. The present study of the chemiluminescent reactions of ozone is limited to those compounds which have a sufficient vapor pressure at room temperature. The types of compounds studied are inorganic (boron trichloride, carbonyl chloride, carbonyl sulfide, nitric oxide, nitrosyl chloride, etc.), organic (acetylene, benzene, ethyl alcohol, carbon tetrachloride, etc.) and organometallic compounds (triethyl boron, diethyl zinc, trimethyl aluminum, etc.).

*Numbers in [] throughout the text represent reference numbers.

EXPERIMENTAL

A conventional fast-flow system suitable for the study of gas phase reactions in the 1 mm pressure region was used for the present study. The apparatus manifold is shown in schematic form in Figure 1. The vapors of the reactants were admixed through a nozzle in a 2-cm-i.d. pyrex tube equipped with quartz windows (Figure 2). However, while studying the reaction of organometallic compounds, it was found that the nozzle became clogged due to the deposition of metallic oxide. The reaction chamber was therefore modified by placing the nozzle upstream in the flow tube of reactant vapors (Figure 3). In this arrangement the nozzle helped in reducing the back diffusion of ozone into the organometallic vapor tube.

A technique as that described by Cook *et al* [25] was used for the handling of ozone. This technique utilizes the sorption process for the separation of ozone. The ozone production and handling system is shown in Figure 4. Oxygen from a cylinder is passed through a silent electric discharge at atmospheric pressure and then through a U tube containing silica gel at the dry ice-acetone temperature ($\sim -80^{\circ}\text{C}$). The ozone produced in the discharge is adsorbed by the cold silica gel and the oxygen is passed to the atmosphere. The adsorption of a sufficient quantity of ozone is indicated by the deep blue color of the silica gel. The discharge and oxygen flow is then stopped and the ozonizer is closed to the atmosphere. The remaining oxygen is then pumped off together with some ozone. The ozone is then desorbed by replacing the dry ice-acetone trap with an ethylene glycol one maintained at -30°C . The desorbed ozone is collected into a 3-liter flask. During the reactions of ozone with various compounds, the ozone flow is controlled by a teflon needle valve into an absorption cell (50-cm length) with quartz windows at both ends. The partial pressure of the ozone, prior to its entry into the reaction tube is measured by the absorption of radiation from a pen ray Hg lamp. It may be noted, however, that the partial pressure of ozone in the reaction chamber is somewhat less than that in the absorption cell.

In order to observe the chemiluminescence, the appropriate flow rates of argon and the reactant vapor were adjusted. The ozone was then introduced into the system through the teflon needle valve. The flow rate of ozone was then gradually increased up to the safe maximum limit. In some cases the chemiluminous glow was observed at the point of mixing of ozone and the reactants. However, for several reactants no chemiluminescence was observed, even when the flow rates of the reactant were varied over the maximum possible range.

The spectra of the chemiluminescent glows were recorded with a Perkin Elmer (Model 99) monochromator equipped with a 600 lines/mm grating and an EMI 9558 Q photomultiplier tube. In order to obtain the relative intensity of spectral features observed in the spectra, the spectral response of the recording system was calibrated by the method described previously [26]. In

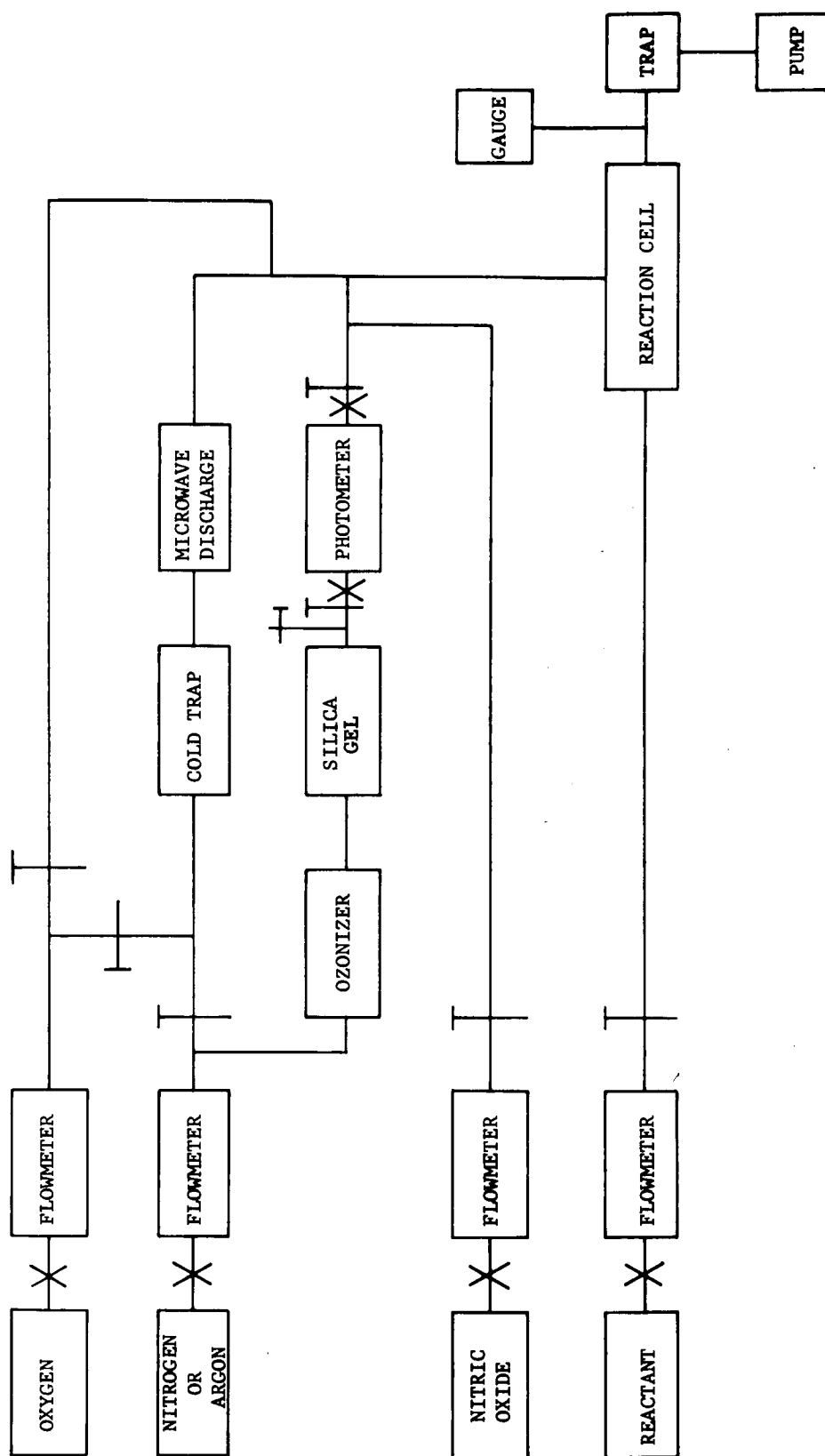


Figure 1. Medium pressure reaction system.

MAGNESIUM
OXIDE
LAYER

QUARTZ
WINDOW

(O, N OR O₃)

McLEOD
GAUGE

TO
PUMPS

LEADS OF
HEATING WIRE

(NO OR NO₂)
(LIQUID VAPOR
REACTANTS)

REACTANT GAS

Figure 2. Low pressure reaction chamber.

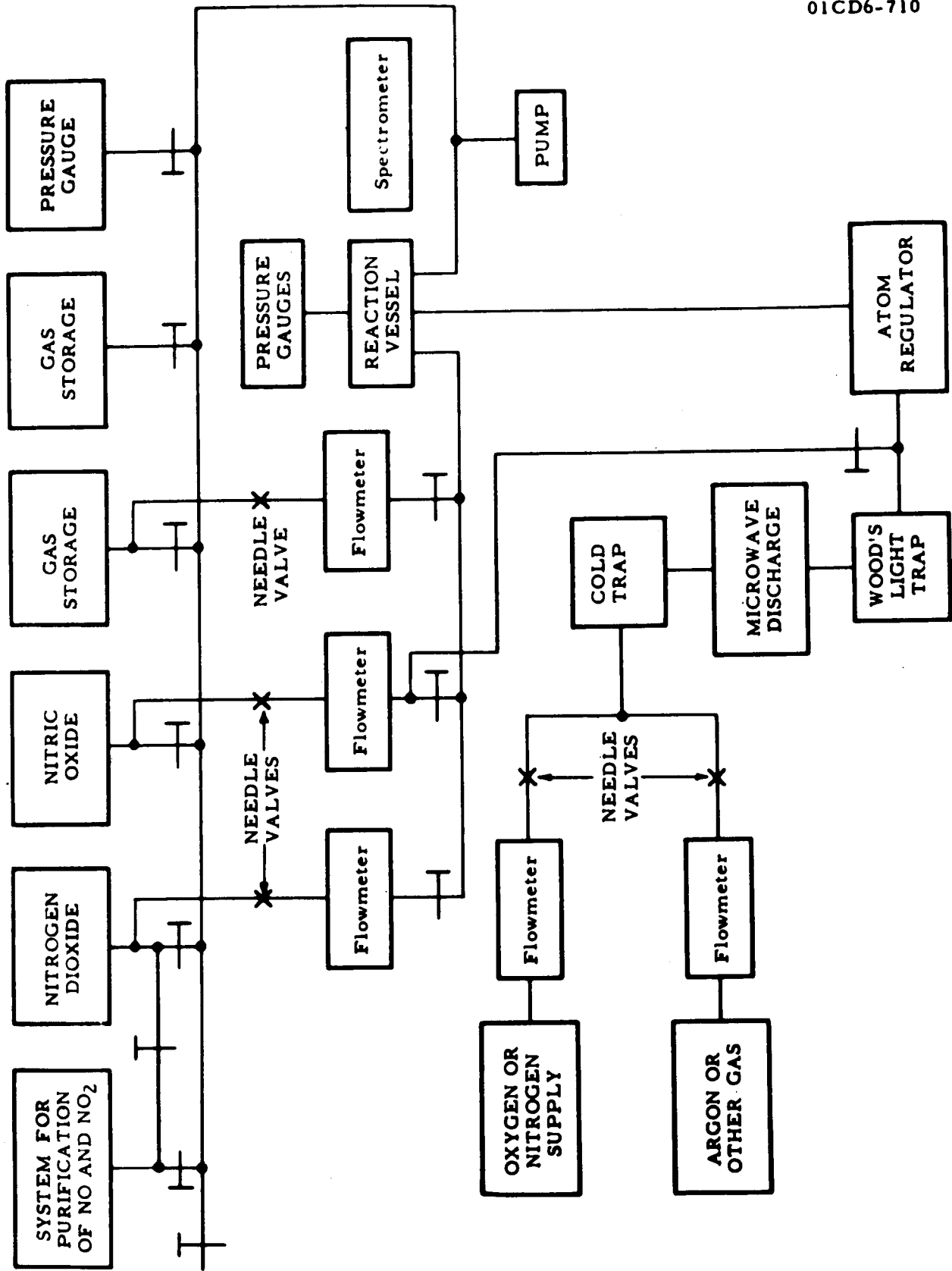


Figure 3. Block diagram of complete apparatus for observation of chemiluminescence.

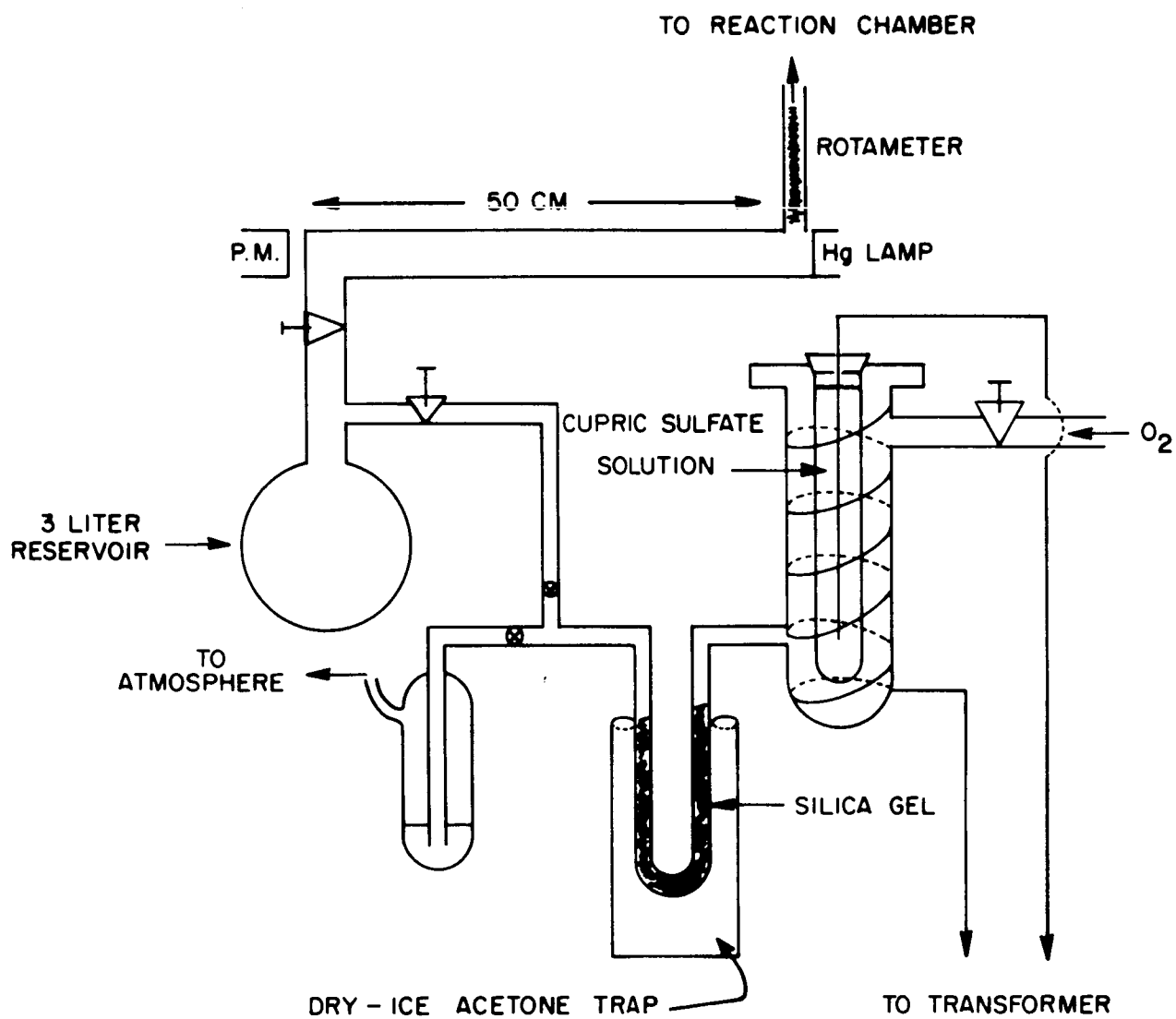


Figure 4. Ozone handling system.

general, the intensity of the chemiluminescence was low and spectra could only be recorded for the chemiluminescent reactions of trimethyl aluminum, diethyl zinc, triethyl boron, ethylene and nitric oxide.

Since all the organometallic compounds studied by us are highly pyrophoric, an arrangement shown in Figure 5 was used for transferring the liquid from its container to the reaction system. The details of the handling procedure are given by Sharma and Padur [27].

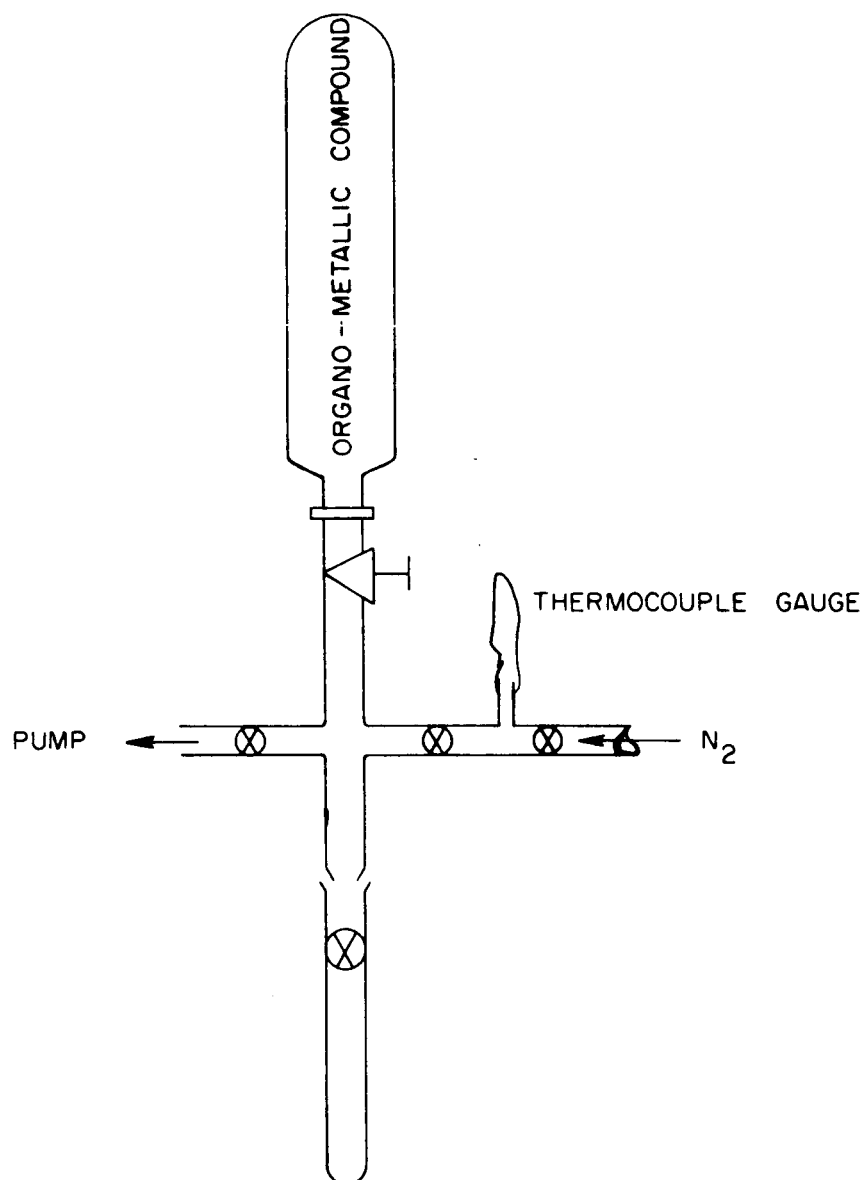


Figure 5. An arrangement for transferring organometallic liquid.

OBSERVATIONS AND DISCUSSIONS

The results of the visual observation of the chemiluminescence produced during the gas phase reaction of several compounds with ozone are summarized in Table 1. The second column in the above-mentioned table indicates the total pressure in the reaction tube, which was due to, predominantly, argon and ozone. The partial pressure of ozone given in column three was measured in the absorption cell at the maximum ozone flow rate. However, the maximum partial pressure of ozone in the reaction tube was somewhat lower than given in Table 1.

The summary of the gas phase chemiluminous reactions of ozone is given in Table 2.

Among the several inorganic compounds studied, only diborane, hydrazine and nitric oxide produced visible chemiluminescence during their reaction with ozone. However, the intensity of the chemiluminescence produced during the reaction of diborane and hydrazine was too low to record the spectrum. The spectrum of the chemiluminescence produced during the reaction of nitric oxide and ozone consists of an apparent continuum starting from 5700\AA to 7100\AA , the limit of the present detector. However, a weak band structure appears to be superimposed over the continuum. Clyne *et al.* [22] have also observed the similar spectra of chemiluminescence produced during the gas phase reaction of NO and ozone. Figure 6 shows the spectra of chemiluminescence observed by us and also shows the relative intensity given by Clyne *et al.* in three wavelength regions, i.e., 6150\AA to 6700\AA , 6700\AA to 7200\AA , and 7200\AA to 7750\AA . The observed spectrum of the chemiluminescence produced by the reaction between NO and O_3 is compared with that produced by the reaction of NO and O. The latter spectrum is given by Fontijn *et al.* [28]. It may be noted that the short wavelength limit of NO + O spectrum is about 4000\AA and that of NO + O_3 is about 5700\AA . The energy difference between the onset of the two spectra is approximately equal to the bond energy of the O - O_2 bond in ozone. In contrast with the spectrum of the chemiluminescence produced by the reaction of NO and O the spectrum of the chemiluminescence produced during the reaction of NO and O_3 shows much stronger vibrational structure. On the basis of the above observation and from the study of its kinetics, Clyne *et al.* [22] have concluded that the following reaction mechanism is operative in the production of chemiluminescence during the reaction between NO and O_3 :

TABLE 1

A SURVEY OF THE GAS PHASE CHEMILUMINOUS REACTIONS OF OZONE

Reactants	Total Pressure in Reaction Vessel	Partial Pressure of Ozone in Absorption Cell (maximum)	Remarks
Acetylene	280 to 700 μ	160 μ	No visible glow
Allene	280 to 1000 μ	230 μ	No visible glow
Benzene	340 to 700 μ	83 μ	No visible glow
Boron Trichloride	280 to 700 μ	175 μ	No visible glow
Carbon Disulfide	320 to 460 μ	200 μ	No visible glow
Carbon Tetrachloride	260 to 340 μ	175 μ	No visible glow
Carbonyl Chloride	360 to 480 μ	230 μ	No visible glow
Carbonyl Sulfide	280 to 1000 μ	230 μ	No visible glow
Diborane	310 to 340 μ	175 μ	Faint white glow
Diethyl Zinc	280 to 330 μ	140 μ	Faint white glow - continuum and OH bands
Ethyl Alcohol	320 to 1800 μ	115 μ	No visible glow
Ethylene	280 to 310 μ	125 μ	Faint white glow - OH bands
Germanium Tetrahydride	170 to 360 μ	230 μ	No visible glow
Hexene	360 to 700 μ	230 μ	Faint white glow
Hexyne	280 to 570 μ	200 μ	No visible glow
Hydrazine	180 to 320 μ	200 μ	Faint glow
Hydrogen Sulfide	340 to 440 μ	200 μ	No visible glow
Methyl Acetylene	280 to 880 μ	160 μ	No visible glow
Nitric Oxide	280 to 620 μ	140 μ	Faint red glow - Continuum & NO ₂ bands
Nitromethane	320 to 550 μ	230 μ	No visible glow
Nitrosyl Chloride	280 to 700 μ	230 μ	No visible glow
Sulfur Dioxide	340 to 550 μ	200 μ	No visible glow
Trichloroethylene	240 to 340 μ	230 μ	No visible glow
Triethyl Boron	280 to 310 μ	110 μ	Greenish glow - BO ₂ bands
Trimethyl Aluminum	260 to 310 μ	125 μ	Whitish glow - Continuum and OH bands
Trimethyl Antimony	260 to 310 μ	200 μ	No visible glow

TABLE 2
THE CHEMILUMINOUS GAS PHASE REACTION OF OZONE

S. No.	Reactant	Intensity (relative)	Remarks
1	Diborane	0.1	No spectral information
2	Diethyl Zinc	0.5	OH band at 3070Å, continuum in the visible region
3	Ethylene	0.1	OH band at 3070Å
4	Hexene	0.1	No spectral information
5	Hydrazene	0.1	No spectral information
6	Nitric Oxide	1.0	Continuum starting from 4000Å and ex- tending into infrared
7	Triethyl Boron	1.5	BO and BO ₂ bands
8	Trimethyl Aluminum	20.0	Continuum starting from 3300Å and ex- tending into infrared

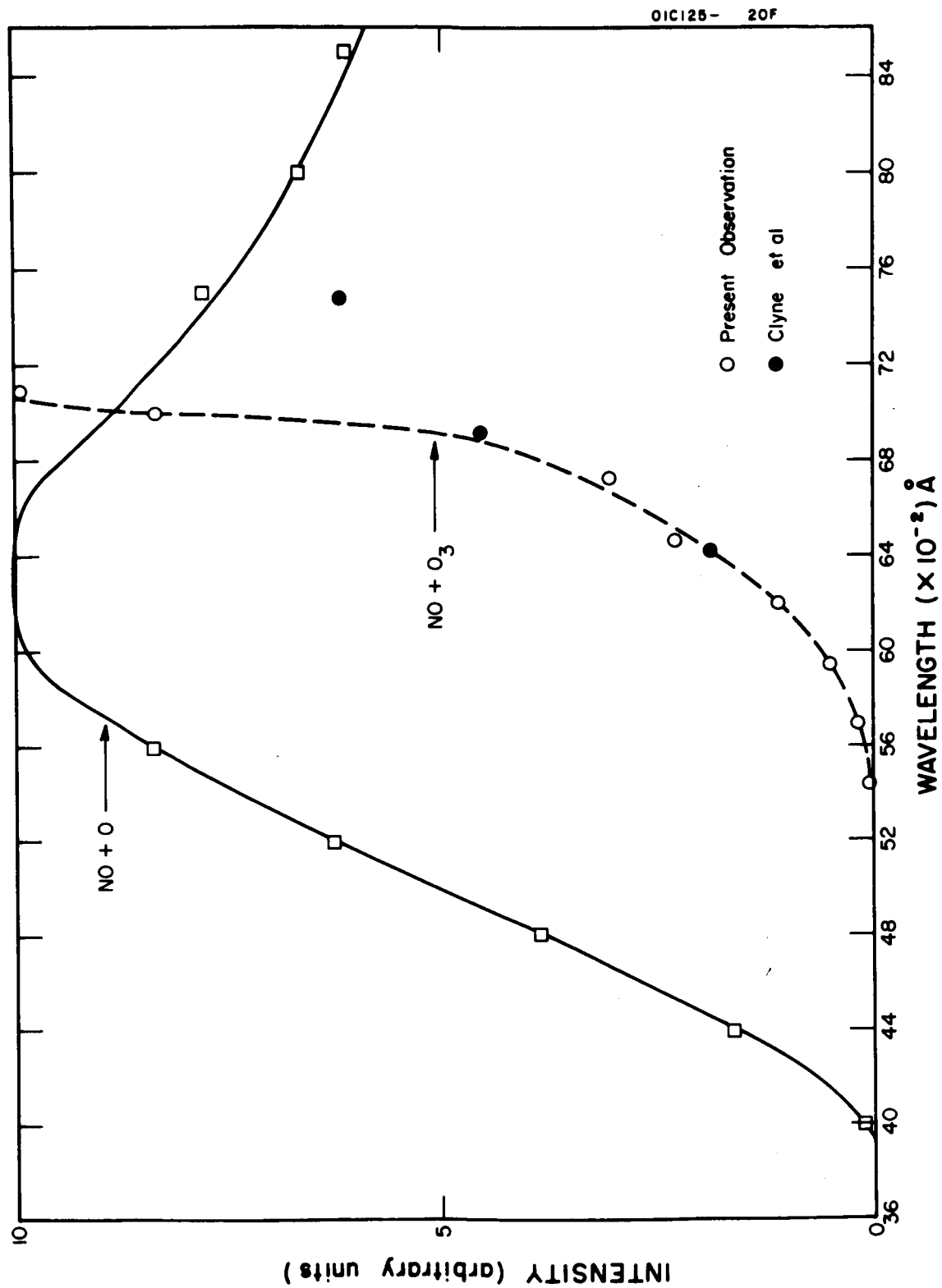


Figure 6. The spectra of chemiluminescence produced during the reaction of nitric oxide with ozone and atomic oxygen.



The rate of consumption of ozone is given by:

$$k' [\text{NO}] [\text{O}_3]$$

with $k' = 8.6 \times 10^{-13} \exp(-2460 \pm 150)/RT \text{ cm}^3/\text{sec}$, and the intensity of chemiluminescence is given by:

$$I = I_0 [\text{NO}] [\text{O}_3]/M$$

with $I_0 = 20.7 \exp(-4180 \pm 300)/RT \text{ sec}^{-1}$ for wavelengths shorter than 8750\AA . It therefore appears that the formation of normal NO_2 and the electronically excited NO_2 proceeds via different potential surfaces because the activation energies for the consumption of O_3 and that for the production of chemiluminescence are different.

Ethylene and hexene are the only compounds among the hydrocarbons studied by us which show faint chemiluminescence. The intensity of the chemiluminescence produced during the reaction of hexene and ozone are too low to obtain a spectrum. However, the intensity of the chemiluminescence produced during the reaction of ethylene was sufficient to record a faint spectrum which indicated the presence of an ultraviolet OH band at about 3100\AA .

The vapors of organometallic compounds, when mixed with ozone, produced stronger chemiluminescence than the compounds of other groups. However, no visible chemiluminescence was observed when trimethyl antimony vapor was mixed with ozone. The intensity of chemiluminescence produced during the reaction of diethyl zinc and ozone was very weak and again a good spectrum could not be recorded. Some indication of the presence of the OH band at about 3100\AA and a weak continuum in the visible region has been obtained. The intensity of the chemiluminescence produced during the reactions of triethyl boron and trimethyl aluminum was sufficient to obtain a good spectrum. It was found that the spectra of chemiluminescence produced during the reactions of triethyl boron and trimethyl aluminum with ozone were similar to the respective

spectra of chemiluminescence produced by their reactions with atomic oxygen. The spectra of the chemiluminescence produced during the reaction of triethyl boron and trimethyl aluminum with atomic oxygen have been reported by Sharma and Padur [27]. They have found that the spectrum of chemiluminescence produced during the reaction of trimethyl aluminum consists of a continuum starting from about 3300 and extending into the infrared and that of triethyl boron consists of discrete bands of BO and BO_2 molecules. It may be noted that the relative intensity of the BO bands with respect to the BO_2 bands in the spectra of chemiluminescence produced during the reaction of triethyl boron with ozone is much less than that with atomic oxygen. The identification of the spectra of chemiluminescence produced during the reaction between triethyl boron and atomic oxygen is given in Table 3.

It is apparent from Table 2 that among the studied gas phase chemiluminous reaction of ozone, the strongest chemiluminescence was observed during the reaction of trimethyl aluminum. The effect of molecular oxygen on the intensity of chemiluminescence produced during the reaction of trimethyl aluminum was investigated by replacing the argon with molecular oxygen. It was found that a diminution of about 10 percent in the intensity of chemiluminescence was observed when the concentration of the molecular oxygen in the reaction tube was of the same order of magnitude as that of ozone.

TABLE 3

THE IDENTIFICATION OF THE SPECTRUM OF THE CHEMILUMINESCENCE
PRODUCED DURING THE REACTION BETWEEN TRIETHYL BORON AND ATOMIC OXYGEN

			Identification*	
S. No.	Measured Wavelength (Å)	Relative Intensity	Wavelength (Å)	Emitter of Transition
1	4150	1.8	4124 - 4145 4162.9 - 4168.9	BO α (2,1) BO ₂ (A \rightarrow X)
2	4340	3.5	4339.4 - 4365.7 4335.0 - 4349.0	BO α (1,1) BO ₂ (A \rightarrow X)
3	4510	6.3	4496.8 - 4506.1	BO ₂ (A \rightarrow X)
4	4690	9.1	4685.8 - 4694.8	BO ₂ (A \rightarrow X)
5	4900	9.2	4891.6 - 4917.0	BO ₂ (A \rightarrow X)
6	5160	7.6	5144.6 - 5183.5	BO ₂ (A \rightarrow X)
7	5430	5.6	5403.8 - 5470.1	BO ₂ (A \rightarrow X)
8	5725	3.2	5766.5 - 5790.7	BO ₂ (A \rightarrow X)

*The wavelength of BO bands are from Pearse and Gaydon [30] and that of BO₂ bands are from Mavrodineanu and Boiteux [31].

CONCLUSIONS

Similar spectral features, observed in the chemiluminescence produced during the reactions of ozone and atomic oxygen indicate that the same reaction is responsible for the production of the excited species. One of the possibilities of the similar reaction in the two cases may be the presence of atomic oxygen produced by the thermal decomposition of ozone. Benson [29] has discussed the thermal decomposition of ozone and has given the following expression for the steady state concentration of atomic oxygen:

$$(O)_{ss} = \frac{k_1 (O_3)(M)}{k_2 (O_2)(M) + k_3 (O_3)} \quad (4)$$

with

$$k_1 = 7.7 \times 10^{-9} \exp(-24000/RT) \text{ cm}^3/\text{sec}$$

$$k_2 = 1.67 \times 10^{-34} \exp(600/RT) \text{ cm}^6/\text{sec}$$

$$k_3 = 4.93 \times 10^{-12} \exp(-6000/RT) \text{ cm}^3/\text{sec}$$

The calculation of the steady state concentration of atomic oxygen produced due to the thermal decomposition of ozone at 300°K shows that its concentration is too small to explain the observed chemiluminescence as due to the reaction between the studied reactants and atomic oxygen produced by the thermal dissociation of ozone. However, larger concentrations of atomic oxygen may be produced as an intermediate product during the reaction between the above reactants and ozone. Benson [29] has indicated that the thermal decomposition of ozone is extremely sensitive to the presence of metals, metal oxide, organic matter, peroxides and oxides of nitrogen. No definite information regarding the gas phase chemical reaction of ozone with the above compounds is available. Therefore, more extensive observations are required to reveal the mechanism responsible for the production of chemiluminescence during the reaction of ozone with the above studied compounds.

REFERENCES

1. Bailey, P. S., Chem. Rev. 58, 925 (1928).
2. Bernanose, A. J. and René, M. G., Ozone Chemistry and Technology: Advances in Chemistry Series 21, 7 (1959).
3. Baker, H. B. and Strutt, R. J., Ber. 47, 1047 (1914).
4. Centnerszwer, M., Z. Phys. Chem. 26, 1 (1898).
5. Chappius, J., Bull. soc. chim. Paris 35, 419 (1881).
6. Zabiezynski, D. and Orlowski, W., Roczniki Chem. 16, 406 (1936).
7. Kautsky, H. and Zocher, H., Z. anorg. Chem. 117, 209 (1921); Z. Elektrochem. 29, 308 (1923).
8. Knauss, H. P. and Murrey, A. E., Rev. Sci. Instru. 11, 78 (1940).
9. Morren, J. F. A., Paggendorf's Ann. 127, 643 (1866).
10. Richarz, F. and Schenck, R., Stizber. k. preuss. Akad. Wiss. 1102 (1908); 490 (1904).
11. Sarrasin, E. Paggendorf's Ann. 140, 425 (1876).
12. Strutt, R. J., Proc. Roy. Soc. A87, 533 (1911); Z. Physik 15, 274 (1914).
13. Trautz, M. and Haller, W., Z. Wiss. Phot. 29, 48 (1930).
14. Trautz, N. and Seidel, W., Ann. Physik 67, 527 (1922).
15. Thorpe, T. H. and Tutton, A. N., J. Chem. Soc. 57, 545 (1890).
16. Otto, N., Compt. rend. 123, 1005 (1896).
17. Biswas, J. and Dhar, N., Z. anorg. Chem. 173, 125 (1928); 199, 400 (1931).
18. Harvey, E. N., J. Phys. Chem. 33, 1456 (1929).
19. Briner, E., Helv. Chem. Acta 23, 320 (1940).
20. Briner, E. and Perrotet, E., ibid. 23, 1253 (1940).
21. Druckney, H. and Richter, R., Z. Physiol. Chem. 29, 158 (1941).
22. Clyne, M. A. A., Thrush, B. A. and Wayne, R. P., Trans. Farad. Soc. 60, 359 (1964).

REFERENCES (continued)

23. Halstead, C. J. and Thrush, B. A., *Nature* 204, 992 (1964).
24. Garvin, D., Broida, H. P., and Kostowski, H. J., *J. Chem. Phys.* 32, 880 (1960).
25. Cook, G. A., Kiffer, A. C., Klumpp, C. V., Malik, A. H., and Spence, L. A., *Ozone Chemistry and Technology: Advances in Chemistry Series* 21, 44 (1959).
26. Sharma, A. and Padur, J. P., GCA Tech. Rpt. No. 65-17-N (1965).
27. Sharma, A. and Padur, J. P., GCA Tech. Rpt. No. 65-19-N (1965).
28. Fontijn, A., Meyer, C. B. and Schiff, H. I., *J. Chem. Phys.* 40, 64 (1964).
29. Benson, S. W., The Foundations of Chemical Kinetics, McGraw-Hill Book Co., 1960.
30. Pearse, R. W. B. and Gaydon, A. G., The Identification of Molecular Spectra, John Wiley & Sons, Inc., New York, 1963.
31. Mavrodineanu, R. and Boiteux, H., Flame Spectroscopy, John Wiley & Sons, Inc., New York, 1965.